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LACK, Craig, D.: 438 Greenwood Drive, Wilmington, DE 19808 (US), LUO, Qiliang: 91-4 Thorn Lane, Newark, DE 19711 (US).

(74) Agent: BENSON, Kenneth, A.: Rodel Holdings, Inc., Suite 1300, 1105 North Market Street, Wilmington, DE 19899 (US).

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(71) Applicant: RODEL HOLDINGS, INC. [US/US]; Suite 1300, 1105 North Market Street, Wilmington, DE 19899 (US).

(72) Inventors: THOMAS, Terence, M.: 209 Cullen Way, Newark, DE 19711 (US), BURKE, Peter, A.: 104 Interlachen Court, Avondale, PA 19311 (US), SACHAN, Vikas: 121 Brook Run, Hockessin, DE 19707 (US).

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(57) Abstract: A slurry solution used in a process for chemical mechanical polishing of metal based layers, such as copper or tungsten. The solution comprises, a buffer that maintains a pH between about 3 and about 10, and an oxidant reacting with the metal based layer to cause a passive oxide film to form that is stable at a pH maintained between about 3 and about 10.

(54) Title: SLURRY SOLUTION FOR POLISHING COPPER OR TUNGSTEN

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SLURRY SOLUTION FOR POLISHING COPPER
OR TUNGSTEN

This invention relates generally to semiconductor processing and, more specifically to a buffered slurry solution for use in the chemical mechanical polishing, CMP, of copper or tungsten.

Chemical mechanical polishing (CMP) is a process in which a polishing pad and slurry are used to remove layers from the upper surface of an in-process semiconductor wafer. Mechanical movement of the pad relative to the semiconductor wafer provides an abrasive force for removing the exposed surface layer of the wafer. CMP is often used to planarize a given layer across an entire wafer. A CMP slurry is a water based system comprising: 1. suspended abrasive particles (to provide mechanical removal); and 2. chemical agents (to provide chemical removal). In CMP slurries, a metal etchant, metal oxidant, and an abrasive agent have been employed. The oxidant reacts with the metal to form a passive oxide layer, which serves to protect the metal from the etchant. The abrasive agent removes the passive oxide layer from the metal layer, allowing the etchant to etch away a portion of the metal layer. Once the metal has been etched, the passive oxide layer forms again. This process continues until the elevated peak portions of the metal layer have been polished away, resulting in planarization. The slurry solutions are acidic and tend to corrode polishing tool components, such as the conditioning end-

effector and any non-plastic parts of the slurry removal system. Thus, there is need for a suitable solution for a CMP slurry for the planarization of copper or tungsten without corroding metal polishing tool components.

The present invention is directed to a solution for use in chemical mechanical polishing of a metal based layer on a semiconductor substrate. The solution comprises; a buffer capable of maintaining the pH of the slurry between about 3 and about 10; and an oxidant capable of causing a passive oxide film to form on the metal. An advantage of the invention is that the passive oxide film is stable at the maintained pH of between about 3 and about 10, and the invention avoids corrosion of the metal based layer and of metal components of a polishing tool.

Embodiments of the invention will now be described by way of example, with reference to the accompanying drawings, according to which:

FIG. 1 shows a prior art set up of a tool for performing CMP processing;
 FIG. 2a shows an in-process wafer before CMP processing of a copper layer

5 formed on the upper surface;

FIG. 2b shows an in-process wafer after CMP processing of a copper layer formed on the upper surface;

FIG 3 shows potentiodynamic scans illustrating the beneficial characteristics of a buffered slurry of the present invention when used on copper;

10 FIG. 4 shows potentiodynamic scans illustrating the beneficial characteristics of a buffered slurry of the present invention when used on copper;

FIG. 5 shows potentiodynamic scans illustrating the beneficial characteristics of a buffered slurry of the present invention when used on tungsten.

As used herein, the term "substrate" refers to any semiconductor substrate, such as, for example, a semiconductor wafer substrate. The term "substrate" may include either a semiconductor wafer or the wafer along with various process layers formed on the wafer. The term "copper" refers to pure copper, as well as copper based metals. Copper based metals include alloys having substantial amounts of silver. Tungsten refers to pure tungsten as well as alloys thereof.

20 In the practice of the present invention, copper based metals may also include a mixed metal layer comprised of metals in addition to copper or a multi-layer stack comprised of one or more copper layers which optionally also includes metal layers other than copper.

A controlled oxide layer (on the metal) is intended to mean an oxide layer or film which forms on a metal layer in the absence of abrasion, creating an effective protective barrier between the metal layer and the corrosive or etching action of a polishing slurry.

Generally, the controlled oxide layer maintains this barrier except during those times when the metal layer is exposed by abrasion during the polishing process.

FIG. 1 shows a typical known set up of a tool for performing CMP processing. A

30 wafer 10 (from which multiple semiconductor devices will be formed) is supported by a wafer carrier 20. The wafer 10 is placed face-down on a polishing pad 30 so that a surface 11, which is to be polished, rests against the surface of pad 30. Wafer carrier 20 is coupled

to equipment that provides for the rotation and movement of wafer 10 relative to pad 30. Pad 30 may also be mounted so as to rotate in operation. Slurry delivery system 40 allows slurry 41 to flow over the surface of pad 30 during the polishing operation.

FIG. 2a and FIG. 2b show a known use of CMP processing to form metal features on a semiconductor wafer. In FIG. 2a, an in-process semiconductor wafer 10 is shown with conductive region 50 disposed on a substrate 12. It will be appreciated that conductive region 50 could alternatively be inset into substrate 12 of the wafer 10, or may rest upon other intermediate layers not shown. A dielectric region 60 is shown with contact pattern 61 formed therein. Metal layer 70 is formed above the upper surface of dielectric region 60 and fills the contact pattern 61. The upper surface 11 of wafer 10 is generally non-planar before CMP processing.

FIG. 2b shows the result of CMP processing performed with equipment like that shown in FIG. 1. At the end of the CMP processing, the upper surface 11 of wafer 10 is generally planar. All that remains of metal layer 70 is a contact 71 formed in contact pattern 61. The technique illustrated in FIG. 2a and FIG. 2b is a well-known application of metal CMP processing to form a metal contact for connecting two conductive regions separated by an insulator. It will be appreciated that there are other possible applications of metal CMP to integrated circuit fabrication, for example metal plugs, metal damascene processes, etc.

The present invention provides a CMP slurry solution based on a passivation type chemistry that is particularly useful in CMP processing of copper features. In general, passivation is achieved by creation of a protective oxide on a metal surface. For example, in the case of copper in the pH range of about 3-10, a Cu_2O / CuO passive oxide or a hydrous oxide (such as $\text{Cu}(\text{OH})_2$) may be typically formed. Significantly, it has been discovered that such oxides are not stable in aqueous solutions having a pH of less than about 4 or greater than about 10. As a result, CMP slurries that are known, as having pH values outside this range, have not been effective in forming copper passivation layers that successfully protect copper surfaces from unwanted etching and dishing problems.

The present invention provides a CMP slurry solution buffered to have a pH of from about 3 to about 10, instead of the known slurries having an acidic pH of less than 3 or the highly basic pH of greater than 10. The embodiments of the present invention do not substantially etch or corrode copper or tungsten surfaces in the absence of abrasive action,

and little or no dishing occurs during the CMP process. The slurry embodiments of the present invention also are less chemically aggressive toward corrosion of metal polishing tool components.

Copper is a reactive metal in the presence of an oxidizer, such as dissolved oxygen, (or at a pH above about 7) and can thereby be thermodynamically unstable in aqueous media. Copper thus is readily passivated upon contact with most aqueous solutions. When exposed to an aqueous CMP slurry of the present invention, copper metal will typically react with the oxidizer or dissolved oxygen until a protective oxide film is formed.

Although a separate oxidizing agent may not be required, depending upon pH, a CMP slurry according to the present invention typically includes an added oxidant of suitable strength in order to accelerate the oxidation process of a metal during a CMP process, so that a passive oxide layer may be continuously reformed at a high rate as it is abraded away. This is true, even when a slurry contains a diluent that is an oxidant capable of forming a passive oxide film on a metal layer. Furthermore, a slurry may include a buffer to maintain a pH of from about 3 to about 10, a corrosion inhibitor (if desired), and a suitably dispersed abrasive.

Suitable oxidizing agents known to those skilled in the art may also be used, for example any of the common oxidizing agents such as nitrates, iodates, chlorates, perchlorates, chlorites, sulphates, persulphates, peroxides, ozonated water, and oxygenated water or other oxidizing agents which will not form precipitates at the proposed pH range may be utilized. In addition, co-oxidants may be added. But, co-oxidants have generally been found to be unnecessary. Oxidizing agents can be used in slurries for CMP at concentrations of about 0.01% to about 7% by weight. Generally they are used at concentrations of about 1% to about 7% by weight. An iodate is a preferred oxidizing agent. Most preferred is potassium iodate at about 2% to about 4% by weight.

Corrosion inhibitors which are substantially free of metal ions may have some beneficial effects and could also be added. Suitable corrosion inhibitors include benzotriazole (BTA), mercapto benzotriazole (MBT), and other corrosion inhibitors typically used with metals such as copper which do not adversely affect the properties of the slurry. The corrosion inhibitor helps to form a barrier layer on the surface of the metal thus preventing static etching of the surface. In addition, certain low molecular weight glycols may be effective corrosion inhibitors as well. Corrosion inhibitors may be effective

at concentrations as low as 0.001% by weight in a CMP slurry. Preferred concentrations are in the range of about 0.01% to about 4% by weight of the CMP slurry.

More preferred is the range of about 0.1% to about 2%.

In the practice of the present invention, suitable buffers may be prepared by

5 combining a weak acid and its conjugate base. Preferred buffers that may be employed in the practice of this invention include acetate and phosphate buffers formed by adding a

suitable amount of potassium hydroxide to acetic or phosphoric acid, respectively. It is also possible to prepare a suitable buffer using acetic acid and potassium acetate. Ammonium

10 hydroxide or tetramethyl-, tetraethyl-, or tetrabutyl- forms of ammonium hydroxide may be used to help eliminate positive mobile ion contamination. A suitable basic buffer having a

pH of about 9 may be prepared by adding ammonium chloride to ammonium hydroxide. Buffers may be prepared in a number of ways, and other suitable buffers known to those

skilled in the art, such as carbonate buffers derived from carbonic acid, may be used in the practice of the present invention. In the preparation of the slurry of one embodiment of the

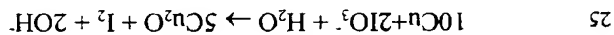
15 present invention, it is preferable to first dissolve oxidizer in deionized water prior to combining the oxidant with the buffer solution due to the acid/base properties of the salt used. A preferred buffer is citric acid/ammonium citrate.

In the practice of the present invention, a relatively hard abrasive is preferred due to

20 the hardness of the protective oxide which is formed on the based metal surface. Alumina, such as alpha- and/or gamma-alumina, or fumed alumina is preferred. However, other suitable abrasives such as, for example, titania, magnesia or polymers may also be

employed. In one embodiment of the present invention, an example mechanism by which an

aqueous oxidant is believed to create a passive oxidation layer on copper is represented by the following equation:



In the practice of the present invention, the amount of oxidant and buffer used in a

slurry composition will depend largely upon the CMP removal rate desired, the type of oxidant and buffer selected, the cost of the oxidant and buffer materials, and the cost of

30 slurry disposal or reclamation. Minimal concentrations of both oxidant and buffer will, as a result, be set by the reasons listed above as well as the need to reduce the level of residual

contamination on process wafers as well as in the fab itself. Typical slurry compositions

contain oxidant present in a range of from about 0.01% to about 7% by weight, and have a buffer present in a concentration of from about 0.1M to about 1M.

Using the slurry compositions as described herein, solutions having a pH of from about 3 to about 10 may be prepared. A preferred pH range is from about 4 to about 6 and most preferred is a pH range of from about 4 to about 5. The pH ranges specified above ensure that a stable passive oxide film, such as copper oxide, is formed on the metal surface being polished. This stable oxide film passivates the metal and reduces the rate of metal dissolution or prevents metal etching completely, thus preventing dishing and allowing smooth surfaces to be formed during the CMP process. Due to the nature of the oxidants employed, the kinetics of the passivation oxidation are rapid. However, during the CMP process, the passivation oxide is removed by abrasion to allow metal removal. Thus, a slurry having a high removal rate and high selectivity in the absence of dishing is provided. In addition, these slurry pH ranges are less chemically aggressive toward metal polishing tool components than the slurry pH ranges of the prior art.

The utilization of potentiodynamic scans such as those provided in FIG. 3 and FIG. 4 provides an electrochemical method for predicting the polishing mechanism of a slurry. As shown in FIG. 3, each potentiodynamic scan 101 and 102 includes an anodic and cathodic curve. The scans can be characterized by identifying and comparing the relative corrosion current and the corrosion potential for each scan. Corrosion current may be approximated by identifying the point where the anodic and cathodic currents are equal in magnitude. However, a more accurate determination of corrosion current may be made by considering all data on both sides of an intersection point and performing a nonlinear least squares fit to the Stern-Geary equation as described in Stern and Geary, J. Electrochem. Soc., 104:56, 1957, which is hereby incorporated by reference. Corrosion potential may be identified as the potential at the intersection point of the curves that form a scan. It has been found that the corrosion current correlates to the static etch rate. More particularly, as the value of the corrosion current decreases, the static etch rate generally decreases. Furthermore, the corrosion potential indicates the amount and completeness of coverage of passivation film formed on the copper (for example, a thin, densely packed passivation layer tends to change the corrosion potential more than a thick, porous layer). A large offset between the corrosion currents and potentials for the with polish scan and the without polish scan is desirable. Further, in the without polish case, it is desirable to have minimal

corrosion (indicating that a stable passivation layer has been formed and no substantial metal dissolution is occurring).

In FIG. 3, scan 1 corresponds to use of a buffered oxidizer solution at pH = 1.27. Scan 2 corresponds to use of a buffered oxidizer solution at pH = 4.64. In FIG. 4, scan 1 corresponds to the use of a buffered oxidizer solution at pH = 6. Scan 2 corresponds to use of a buffered oxidizer solution at pH = 2.5. The potentiodynamic scans in both FIG. 3 and FIG. 4 reveal that slurry formulations of the present invention allow a stable copper passivation layer to form and achieve a passivation type of chemistry when the pH is >3 and not passivated when the pH is <3. This is indicated by the difference in the corrosion current density. As shown in FIG. 3, when the slurry pH increases from pH 1.3 to pH 4.6, the calculated corrosion current density decreased from 14.9 mA/cm² to 14.2 uA/cm². A passivation film was formed on copper when the pH is greater than pH 4.5. Any Icorr (static etch rate) less than 20 uA/cm² can be used for copper CMP without causing significant recess during polishing. As shown in FIG. 4, when the slurry pH increases from pH 2.5 to pH 6.0, the corrosion current density decreased from 33.85 uA/cm² to 6.58 nA/cm². The copper surface is passivated when the pH is greater than pH 4.5, such as pH 6.0. Any Icorr less than 20 uA/cm² can be used for copper CMP without causing significant recess during polishing.

FIG. 5 shows that desirable passivation characteristics similar to those achieved with copper may also be achieved with tungsten using a buffered aqueous ammonium oxidizer solution having a pH of about 4.0.

An advantage of the invention is that a slurry solution for polishing copper or tungsten based metal on a wafer provides a passive oxide film that is stable at a pH of between about 3 and about 10, as maintained by a buffer, and corrosion is avoided of the copper or tungsten based metal and of metal components of the polishing tool.

Claims:

1. A solution for use in chemical mechanical polishing of a copper or tungsten based layer on a semiconductor substrate, said solution comprising:

5 a buffer maintaining the pH of the solution between about 3 and about 10; and an oxidant reactive with the copper or tungsten base layer to provide a passive oxide film to form on the copper or tungsten based layer at said pH of the solution, said

oxidant comprising a separate oxidizing agent in said solution.

2. The solution of claim 1, wherein the pH of the solution is further adjusted

between about 4 and about 6.

3. The solution of claim 1, wherein the separate oxidizing agent comprises

ammonium iodate.

4. The solution of claim 3, wherein a concentration of ammonium iodate in said

solution is from about 0.01% to about 5% by weight.

5. The solution of claim 1, wherein the buffer comprises at least one of acetic acid,

15 phosphoric acid, carbonic acid, ammonium chloride, citric acid or a mixture thereof mixed with at least one of potassium hydroxide, potassium acetate, ammonium hydroxide,

tetramethyl-ammonium hydroxide, tetraethyl-ammonium hydroxide, tetrabutyl-ammonium

hydroxide, ammonium citrate or a mixture thereof.

6. The solution of claim 5, wherein the buffer is present in the solution in a

20 concentration of from about 0.1M to about 1M.

7. The solution of claim 1 wherein, the oxidant comprises an ammonium iodate

oxidant, and the buffer maintains a pH of between about 4 and about 9.

8. The solution of claim 7, wherein a concentration of ammonium iodate in said

solution is from about 0.01% to about 5% by weight.

25 9. The solution of claim 7, wherein the buffer comprises at least one of acetic acid,

phosphoric acid, carbonic acid, ammonium chloride, citric acid or a mixture thereof mixed with at least one of potassium hydroxide, potassium acetate, ammonium hydroxide,

tetramethyl-ammonium hydroxide, tetraethyl-ammonium hydroxide, tetrabutyl-ammonium

hydroxide, ammonium citrate or a mixture thereof.

30 10. The solution of claim 9 wherein, the buffer is present in a concentration of from

about 0.1M to about 1 M.

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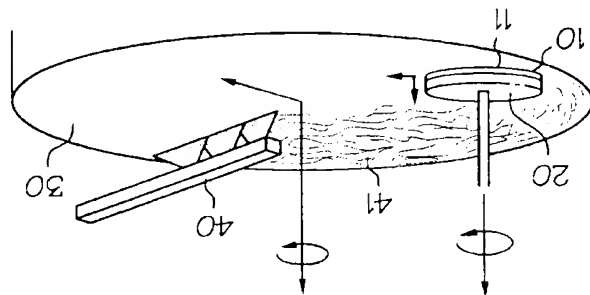


FIG. 1
(PRIOR ART)

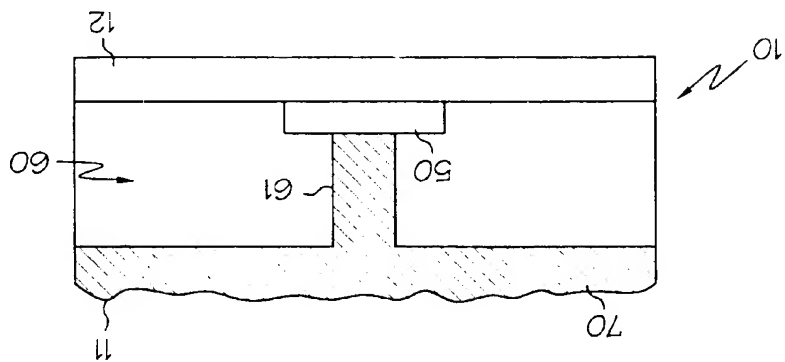


FIG. 2a
(PRIOR ART)

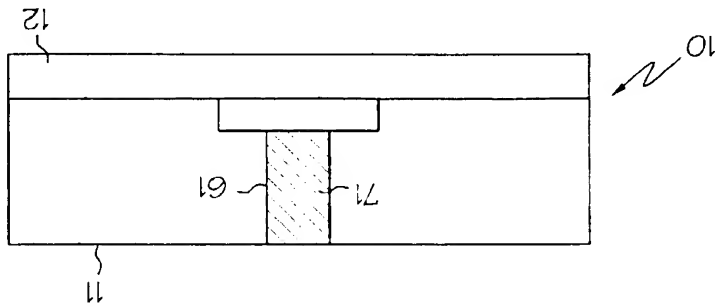


FIG. 2b
(PRIOR ART)

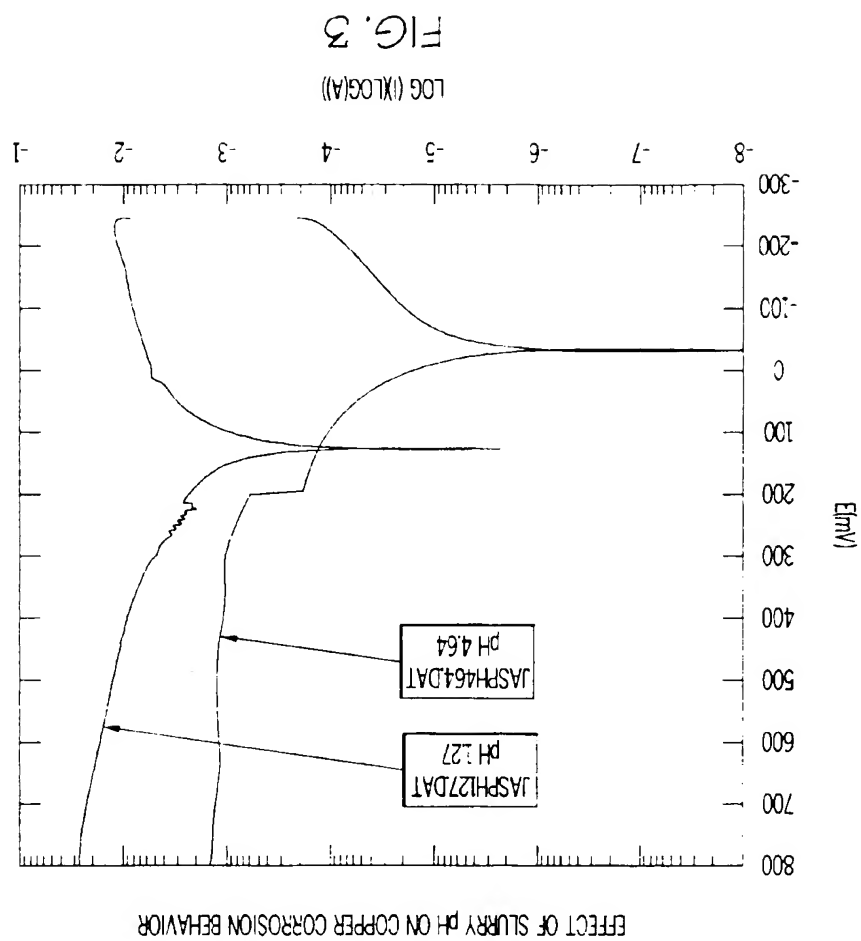


FIG. 3

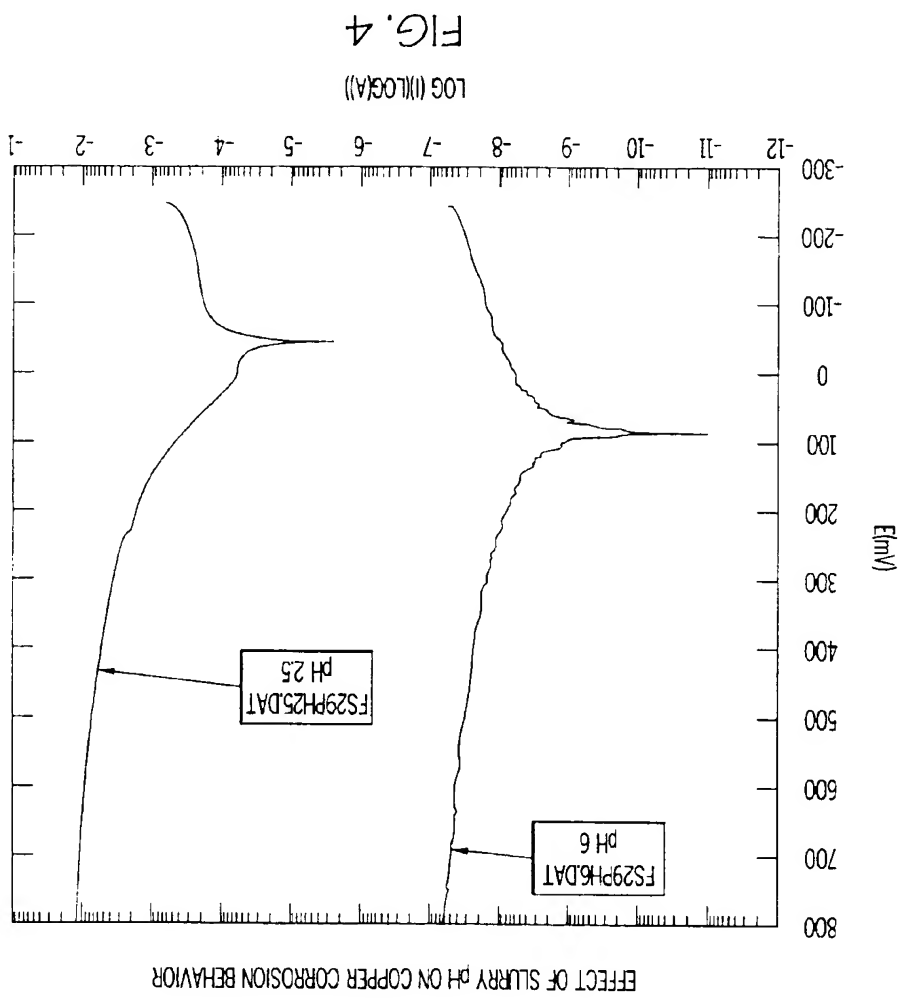
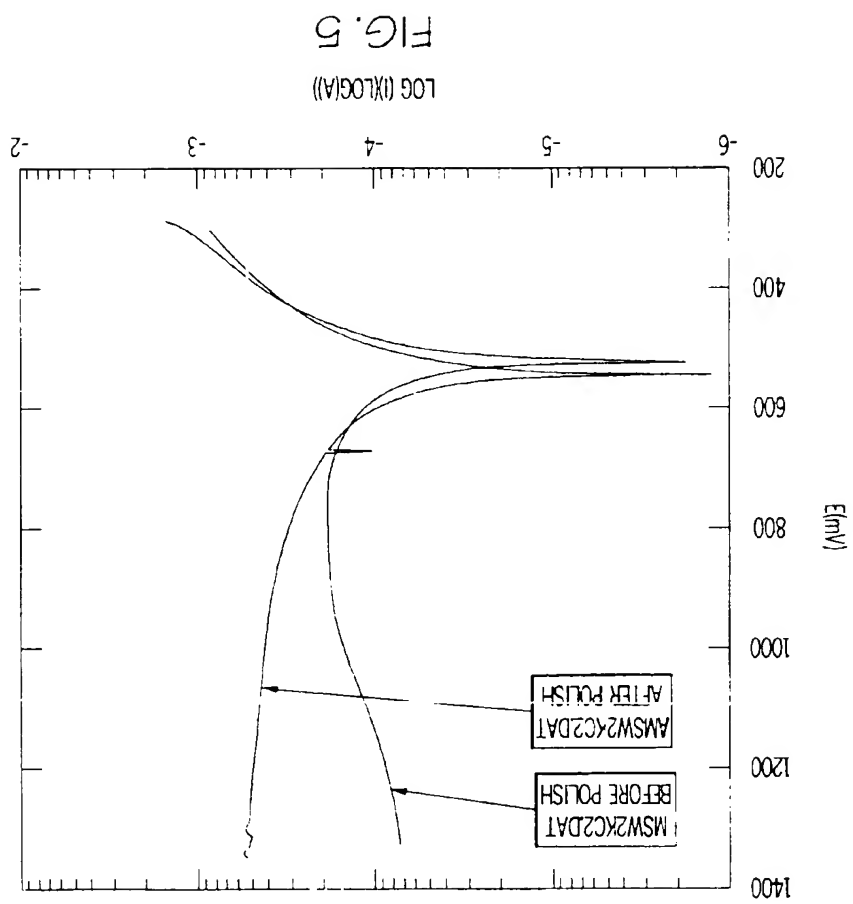


FIG. 4

EFFECT OF ABRASION ON TUNGSTEN CORROSION BEHAVIOR



INTERNATIONAL SEARCH REPORT

Int'l. Application No
PCT/US 00/25221

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09G1/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09G H01L C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 340 370 A (FELLER DANIEL A ET AL) 23 August 1994 (1994-08-23) column 6, line 50 - column 7, line 11 column 7, line 35-63 ----- WO 98 42791 A (ADVANCED MICRO DEVICES INC) 1 October 1998 (1998-10-01) page 4, line 27, 28 page 9, line 25-32 -----	1, 2, 5
A		1

Further documents are listed in the continuation of box C. ☐ Patent family members are listed in annex. ☒

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
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Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Mittler, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/25221

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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